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Kinetic Phase Transitions in Catalytic Reaction Models

Abstract

We review and augment recent developments in the understanding of microscopic lattice gas models for irreversible surface reactions where diffusion does not play a dominant role. Monomer-monomer reactions exhibit domain coarsening much slower than equilibrium Lifschitz-Cahn-Allen coarsening and instead reflect Voter model behavior. The monomer-dimer reaction is of particular interest as a model for CO oxidation. We provide a sophisticated characterization of the associated first- and second-order kinetic phase transitions (corresponding to poisoning) via 'epidemic analyses'. Here one considers the evolution of reaction starting from an empty patch embedded on an otherwise poisoned surface.

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Kinetic Phase Transitions in Catalytic Reaction Models

J. W. Evans

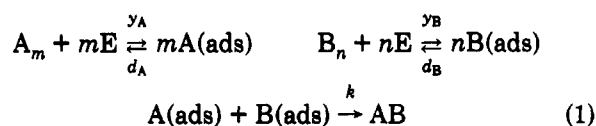
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We review and augment recent developments in the understanding of microscopic lattice-gas models for irreversible surface reactions where diffusion does not play a dominant role. Monomer-monomer reactions exhibit domain coarsening much slower than equilibrium Lifschitz-Cahn-Allen coarsening and instead reflect Voter model behavior. The monomer-dimer reaction is of particular interest as a model for CO oxidation. We provide a sophisticated characterization of the associated first- and second-order kinetic phase transitions (corresponding to poisoning) via "epidemic analyses". Here one considers the evolution of reaction starting from an empty patch embedded on an otherwise poisoned surface.

I. Introduction

In this contribution, we shall describe the behavior of Langmuir-Hinshelwood surface reactions^{1,2} of the type



Here A and B denote distinct atomic constituents of the adsorbing molecules, E represents empty surface sites, and we consider only $1 \leq m, n \leq 2$. The AB_2 model ($m = 1, n = 2$) is of particular interest as a model for CO oxidation (A represents CO, and B_2 represents O_2). For m or $n = 2$, one samples adjacent pairs of sites and adsorbs only if both are empty. The impingement rates are always normalized so that $\gamma_A + \gamma_B = 1$. Our focus is on elucidating kinetic phase transition behavior (usually associated with catalytic poisoning) in such models where diffusion does not play a dominant role.³⁻²²

Traditional chemical kinetics ignores all spatial correlations, thus obtaining coupled rate equations for the

species coverages θ_A and θ_B .^{1,2} Such equations typically only become exact in the limit of high surface diffusion. Nonetheless, they often provide valuable insight into the kinetics, as described below. However, here we emphasize recent more sophisticated analyses using microscopic lattice-gas models.³⁻²² In these, it is necessary to concisely specify which microscopic diffusion processes are operative. The objective of this approach is to provide an understanding of reaction kinetics and kinetic phase transitions at a level of sophistication achieved previously for phase transitions in equilibrium systems (e.g., lattice-gas models of commensurate adlayer ordering). We shall often consider processes without diffusion or (nonreactive) desorption as a first step to elucidating the more general processes. By way of motivation, we note that the diffusionless, desorptionless monomer-dimer (AB_2) model describes reasonably well the experimental CO_2 production rate behavior for CO oxidation on Pt(210) and Pt(111).³

In section II, we begin with the exact hierarchy of rate equations for these processes and discuss results from various approximations to these. The AB model ($m = n = 1$) without diffusion or (nonreactive) desorption is discussed in section III. Although it displays no nontrivial phase transition, it does exhibit complicated "reactive coarsening" behavior. In section IV, we describe in detail the first- and second-order transitions found in the AB_2 model ($m = 1, n = 2$) without diffusion or desorption. Finally, effects of introducing diffusion, nonreactive desorption, interactions, etc., are described in section V. Some concluding remarks are made in section VI. Our discussion is restricted to processes on a square lattice (unless otherwise stated).

II. Rate Equations: Exact Hierarchies and Approximations

Exact rate equations for species concentrations, and for probabilities of multisite configurations to which they couple, can be developed for any specific microscopic model. One must include gain (loss) terms for each way in which configurations can be created (destroyed) by microscopic events. For convenience below we denote probabilities of configurations by the configurations themselves. Thus A denotes θ_A , B denotes θ_B , AB denotes the probability of finding an adjacent AB (as distinct from BA) pair, etc. Conservation of probability implies that $A + B + E = 1$, $AA + BB + EE + 2AB + 2AE + 2BE = 1$, etc. For a square lattice, one obtains the following equations.

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AB Model ($m = n = 1$). One finds that

$$\begin{aligned} d/dt A &= y_A E - d_A A - 4kAB \\ d/dt B &= y_B E - d_B B - 4kAB \end{aligned} \quad (2)$$

Thus for $d_A = d_B = 0$, one obtains $d/dt (A - B) = (y_A - y_B)E \rightarrow 0$, as $t \rightarrow \infty$. Thus the process A poisons (B poisons) with $E \rightarrow 0$, when $y_A > y_B$ ($y_A < y_B$). In section III, we discuss the case $y_A = y_B = 1/2$ (with $d_A = d_B = 0$ and no diffusion) where A and B domains coarsen so again E and $AB \rightarrow 0$, as $t \rightarrow \infty$.

A₂B₂ Model ($m = n = 2$). If $d_A = d_B = 0$, one finds that

$$d/dt A = 2y_A EE - 4kAB \quad d/dt B = 2y_B EE - 4kAB \quad (3)$$

so $d/dt (A - B) = (y_A - y_B)EE \rightarrow 0$, as $t \rightarrow \infty$. A key difference here from the AB model is the occurrence of "jammed" steady, adsorbing states (cf. ref 23) with no EE or AB pairs.

AB₂ Model ($m = 1, n = 2$). If $d_A = d_B = 0$, one finds

$$d/dt A = y_A E - 4kAB \quad d/dt B = 2y_B EE - 4kAB \quad (4)$$

so $d/dt (A - B) = y_A E - 2y_B EE \rightarrow 0$, as $t \rightarrow \infty$. Thus a nontrivial reactive steady state is possible (and exists) for a range of $y_A/y_B (= 2EE/E)$. It is bordered by a second-order transition to a B-poisoned state at "low" $y_A = y_1$, and a first-order transition to an A-poisoned state at "high" $y_A = y_2$ (see section IV).

To elucidate this $d_A = d_B = 0$ behavior, note that the total (reactive) desorption rates for A and B are equal, so total adsorption rates must be equal in a steady state. Thus $y_A = y_B$ is necessary (but not sufficient) in the AB model. However, for the AB₂ model, the adlayer statistics (specifically EE/E) can adjust to some extent to equalize total adsorption rates for a finite range of y_A . Finally, we recall that diffusion terms appear only in the rate equations for multisite configurations. Also, we emphasize that exact analysis of these equations is not possible. This is true even for irreversible adsorption with no reaction or diffusion with m or $n = 2$ on a two-dimensional lattice.²³

Next we discuss the special cases of adsorption-limited ($k = \infty$) and reaction-limited ($k = 0+$) processes. When $k = \infty$, the equations are complicated by the requirement that no AB pairs exist. They have been described in detail for the so-called ZGB model⁷—the diffusionless AB₂ model with $d_A = d_B = 0$. Here we just note that in general the $d/dt (A - B)$ equations remain as in the finite k cases, so the above conclusions regarding steady-state behavior still apply. When $k = 0+$, rate equations for evolution on the infinitely slow time scale $\tau = kt$ are desired. Since such equations have not been developed previously, here we consider the diffusionless AB model with $d_A = d_B = 0$. Reactive coarsening was first observed for this model with $y_A = y_B = 1/2$.²⁴ One finds after accounting for all ways of creating and destroying A, B, AB, etc. configurations on a completely covered surface that

$$d/d\tau A = -d/d\tau B = 4(y_A - y_B)AB$$

$$\begin{aligned} d/d\tau AB &= y_A(ABB + 2_{BB}^A - ABA - 2_{AB}^A) + \\ &\quad y_B(AAB + 2_{AA}^B - BAB - 2_{AB}^B) \\ &\quad : \end{aligned} \quad (5)$$

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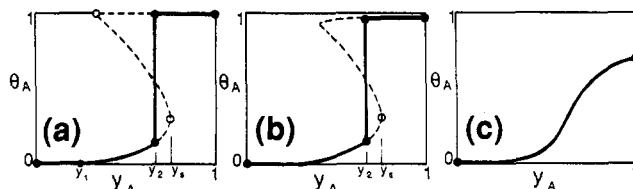


Figure 1. Schematic "phase diagrams" for the AB₂ model showing steady-state A coverage vs y_A for (a) zero, (b) low, and (c) high, nonreactive desorption rates. Solid lines show actual behavior. Dashed lines show MFT predictions, if qualitatively distinct.

from which it is clear that A (B) poisoning occurs for $y_A > y_B$ ($y_A < y_B$).

Traditional chemical kinetics assumes that all multi-site configuration probabilities factor as products of corresponding site probabilities, i.e., species coverages. We call this the site approximation.^{7,10} Thus, all spatial correlations are ignored (adsorbed species are assumed randomly distributed). For $k < \infty$, this case can be realized as the limit of infinite diffusion rates, so solutions of these equations must be well-behaved. The resulting coupled nonlinear equations for species concentrations have been analyzed extensively by applying techniques from the qualitative theory of differential equations.^{1,2} This reveals the existence of multiple steady states (and associated hysteresis phenomena) for $m = 1, n = 2$, but not for $m = n = 1$, or $m = n = 2$. These states constitute the kinetic analogue of the van der Waals loop (see Figure 1) and reflect the existence of a first-order kinetic phase transition in the microscopic AB₂ model (discussed in section IV). The qualitative theory also shows that site-approximation rate equations do not produce self-sustained oscillations in any of these models.^{1,2} Such behavior requires additional nonlinear feedback.¹ Finally we note that the $k = \infty$ AB₂ (or ZGB) model rate equations in the site approximation also exhibit multiple steady states.⁷ These equations cannot be realized as a limit of infinite diffusion and do produce slightly unphysical behavior ($B \approx 0.002$ in some A-poisoned states).⁷

For the AB₂ model with $d_A = d_B = 0$ and $k > 0$ or $k = \infty$, the above site approximation does reasonably well near the A-poisoning transition in predicting steady-state coverage and reaction rate behavior. However it does not predict the B-poisoning transition. This motivated consideration of more sophisticated approximations to the exact rate equations that incorporate explicitly the statistics of pairs or larger ensembles of sites⁷⁻¹⁰ in the spirit of cluster or Kikuchi approximations of equilibrium theory.²⁵ Such approximations succeed in predicting the B-poisoning transition and appear to describe behavior near the A-poisoning transition more accurately. However, we shall reveal some significant limitations of this approach directly below, and again in section IV.

Approximations of the above refined mean-field type for AB₂ models often generate van der Waals type curves, thus directly predicting the location of a spinodal, y_1 , above the A-poisoning transition, y_2 , but not y_2 itself (see Figure 1). Furthermore, there is no simple free energy minimization type criterion or even a Maxwell-type construction to predict y_2 (but see ref 11). Dickman⁷ proposed a kinetic criterion based on the evolution of a lattice a fraction f of which is initially A-poisoned, and the rest is empty. Although results for $f = 1/2$ seem reliable,^{7,9,10} they depend on f and should be questioned.¹⁰ Recently a more

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sophisticated inhomogeneous mean-field-type treatment has been used to predict y_2 based on the evolution of the boundary between the A-poisoned and reactive phase (at least for models with desorption).⁸ Again results seem promising. However, in section IV we show that mean-field-type predictions of y_s are surprisingly poor, which leads us to question even this refined procedure for predicting y_2 . Below we describe all site, pair, ... approximations as mean-field-type theories (MFT).

III. AB-Type Models without Diffusion or Desorption

Since the AB model "quickly" poisons at a rate proportional to $|y_A - y_B|$ when $y_A \neq y_B$, clearly nontrivial kinetic phase transitions are not possible. However, when $y_A = y_B = 1/2$, detailed simulations reveal very slow coarsening of the A and B domains in a quasi steady state obtained rapidly from an initially empty lattice.^{5,12,13,24,26} This coarsening is due to spatial fluctuations in the probabilities of adsorbing A's and B's.¹² To quantify this coarsening, we monitor the decay of concentrations of E, AE, and BE if $k > 0$ (and also AB if $k < \infty$). We find that the decay of any of these quantities can be effectively represented by the form t^{-w} with $w = 0.055 \pm 0.015$ or by $(\ln t)^{-\sigma}$ with $\sigma \approx 0.3$ for finite or infinite k . In contrast we note that the "site approximation" for $k > 0$ predicts a steady state with $A = B = (8k)^{-1} [(8k + 1)^{1/2} - 1]$, and the pair approximation for $k = 0+$ predicts AA, BB, and AB $\rightarrow 1/4$.

It is natural to compare the "reactive coarsening" in these systems with conventional surface-tension-driven Lifshitz-Cahn-Allen (LCA) coarsening in equilibrium systems.²⁷ LCA predicts that the density of domain boundary sites decays like $t^{-1/2}$. Another perspective on this behavior comes from consideration of a blob of one phase or order embedded in a sea of the opposite phase. LCA predicts that the blob size (number of sites) decreases linearly in time.²⁸ Thus for AB models with $y_A = y_B$, we naturally consider the evolution of an A blob embedded in a B sea (separated by a wall of empty sites if $k = \infty$). We find that the average blob size is either roughly constant or slowly increasing for various k (our statistics are poor). However, the survival probability of the blob decreases with time like $t^{-\delta}$ with $\delta = 0.80 \pm 0.20$ independent of k , reminiscent of critical behavior in epidemic models²⁹ (see section IV).

The equation $d/dt(A - B) = (y_A - y_B)EE$, for the A_2B_2 model without desorption looks rather similar to the equation $d/dt(A - B) = (y_A - y_B)E$, for the corresponding AB model. However, these models exhibit rather different behavior because of the above-mentioned possibility for jammed steady states in the A_2B_2 model with $EE = AB = 0$. Here we only discuss the $k = 0+$ reaction-limited case of the A_2B_2 - model with $y_A = y_B = 1/2$, starting from a completely filled lattice ($A + B = 1$). Here AB pairs are removed and immediately replaced by AA or BB pairs, with equal probability. This model is equivalent to the Voter model, for which it is known rigorously that no non-trivial steady states exist, and that coarsening occurs (in

two dimensions).³⁰ This property is related to the recurrence of a simple random walk (in two dimensions).³⁰ Finally, we note that the Voter model is also achieved in the $k = 0+$ limit of the AB_2 model. The only complication here is that one must have $y_A = y_B/4$ in order to ensure a balance in A and B filling rates. (Consider filling an empty pair created by AB desorption. If A is chosen to impinge on one of the empty sites, then it is guaranteed to adsorb. Furthermore, the neighboring isolated empty site will necessarily also be immediately filled by another A. However, if a B_2 is chosen to impinge on one of the empty sites, then there is only a $1/4$ chance that it will have the correct orientation to land on the empty pair.) We exploit this observation in the next section.

IV. AB_2 Model without Diffusion or Desorption

As indicated in section II, the most distinctive features of this model are as follows: a second-order transition from a reactive steady state to a B-poisoned state as y_A drops below y_1 ; a first-order transition to an A-poisoned state as y_A increases above y_2 . For $k = \infty$ (the ZGB model), one finds $y_1 = 0.39065 \pm 0.00010^{14}$ and $y_2 = 0.525 \pm 0.001$.^{4,10,13} As k decreases to $0+$, y_1 and y_2 both approach 0.2 (the width of the reaction window vanishes) as explained in section III. We discuss the two transitions separately.

Second-Order B-Poisoning Transition. As noted above, this transition is predicted by pair and higher order MFT approximations. However, such approximations cannot adequately describe the long-wavelength fluctuations near this transition or predict the critical exponents $\beta_A \geq \beta_B$ defined by $\Theta_A \sim (y_A - y_1)^{\beta_A}$ and $1 - \Theta_B \sim (y_A - y_1)^{\beta_A}$. Simulations for the $k = \infty$ ZGB model predict $\beta_A = 0.69$,⁵ 0.60 ± 0.15 ,¹⁵ and $\beta_B = 0.61$,⁵ 0.63 ± 0.03 ¹⁵ compared with the mean-field value of $\beta = 1$. It is now believed that, near y_1 , this two-component model behaves like the one-component Reggeon spin system, and so is in the universality class of Reggeon field theory (RFT)/directed percolation,²⁹ or the contact model,³⁰ with $\beta_A = \beta_B = \beta = 0.59$. This result apparently still holds if anisotropy in reaction and B_2 adsorption is introduced.¹⁶

An independent analysis of this critical behavior follows from consideration of an empty patch embedded in a B-poisoned sea. With $\Delta_1 = y_A - y_1$, comparison with RFT suggests that for $\Delta_1 \geq 0$ the survival probability, $P_s(t)$, and average number of empty sites, $N_e(t)$, of this nonpoisoned patch should scale like^{14,29}

$$P_s(t) \sim t^{-\delta} \phi(\Delta_1 t^{1/\nu}) \quad \text{and} \quad N_e(t) \sim t^\eta f(\Delta_1 t^{1/\nu}) \quad (6)$$

where $\phi(x) \sim x^{\nu\delta}$ and $f(x) \sim x^{\nu(2-\eta)}$, as $x \rightarrow \infty$. Simulations indicate $\delta \approx 0.452 \pm 0.008$ and $\eta \approx 0.224 \pm 0.010$, again compatible with RFT values.¹⁴

In the contact model, adsorption occurs at empty sites at rate y , and desorption occurs at filled sites with $m \geq 1$ empty neighbors at rate md . A continuous poisoning transition occurs for sufficiently small d/y .³⁰ At least for $k = \infty$, simple physical arguments indicate why the AB_2 model near y_1 exhibits contact model behavior. One argues that the primary role of the A species is to provide a mechanism for B desorption:¹⁷ B's with $m \geq 1$ empty neighbors desorb at a rate cy_A , where c is not equal to m but is simply determined by the local environment. It remains to argue that the presence of A on the surface and the two-site adsorption rule for B_2 do not significantly effect the B-adsorption rate. Let $\rho_A \sim (y_A - y_1)^{\beta_A - \beta_B}$, ρ_E and $\rho_{EE} =$

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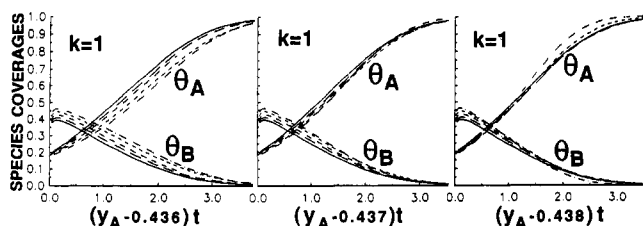


Figure 2. Scaling of the A-poisoning kinetics for $y_A \approx y_s$ in the $k = 1$ AB_2 model with no diffusion or desorption. Curves correspond to y_A values of 0.46, 0.455, 0.45, 0.445, and 0.4425 (from top to bottom for θ_A in the left frame).

$y_A \rho_E / 2y_B$ denote densities of A, E, and EE on the non-B-poisoned surface, respectively. Although $\rho_A \rightarrow 0$ if $\beta_A = \beta_B$, clearly ρ_E / ρ_A and $\rho_{EE} / \rho_A \rightarrow 0$, so the total B-adsorption rate essentially behaves like $y_B(1 - \theta_B)$, as required. Clearly y_A / y_B plays the role of d/y above.

Failure of mean-field-type theories also prompted the development of sophisticated perturbation theoretic treatments for second-order kinetic phase transitions in various one-component models.¹⁷ Finite-size scaling analyses have also been successfully applied to such models.¹⁸

First-Order A-Poisoning Transition. We have noted that this transition is reflected in the MFT rate equations by multiple steady states and hysteresis. Since an initially empty lattice should poison when y_A exceeds, y_2 , one can determine y_2 by direct simulation. However, metastability against nucleation of the A-poisoned phase^{4,12} for $y_2 < y_A < y_s$ causes practical difficulties with this procedure. Indeed we believe that a y_A value of 0.5277 ± 0.0002 estimated for y_2 for $k = \infty$ in ref 5 is closer to y_s than y_2 (see below). These difficulties can be avoided by starting with a lattice that is partly covered by the A-poisoned phase.⁴ Another approach is discussed below. Finally, we note that a cluster size study for $k = \infty$ indicates that the percolation of A and E clusters does not occur for $y_A \leq y_2$; B clusters cease to percolate at $y_A \approx 0.51$.¹⁹ Thus percolation does not correlate simply with the phase transition.

As the kinetics near y_2 is strongly influenced by metastability it is important to determine y_s and thus the width of the metastable region. Analytic extension (extrapolation) of steady-state θ_A and θ_B above y_2 to the point where their slopes simultaneously diverge determines y_s .¹⁰ However, practically it is easier to analyze the kinetics above y_2 . Although the asymptotic behavior is clearly determined by $y_A - y_2$, evolution for $y_A \gtrsim y_s$ for "moderate" times should primarily depend on $(y_A - y_s)t$, i.e., $\theta_A \sim F[(y_A - y_s)t]$. The quality of such scaling of simulation data is very sensitive to the choice of y_s . We thus find $y_s = 0.5292 (0.4371) \pm 0.0005$ for $k = \infty$ (1), very close to but unambiguously above y_2 values (Figure 2). These y_s values are far below the pair-approximation estimates of 0.561 (0.461) for $k = \infty$ (1), and this brings into question the apparent success of MFT in predicting y_2 .

Next we comment in detail on the kinetics near y_2 , noting the expected limitations of MFT. For $y_2 < y_A < y_s$, a dilute A state quickly evolves toward a metastable reactive state—as predicted by MFT—but thereafter undergoes a slow nucleation-mediated A poisoning. Fluctuations in the metastable reactive state must produce an A-poisoned island above a critical size at which the "probability of growth", P_s , becomes significant.³¹ (We comment below on imprecision in the definition of P_s .) Of course here there is no free energy framework for evaluating this critical size or the nucleation rate. We are currently exploring alternatives.

Table I. k Dependence of the Transition Location, y_2 , and Critical Exponents, δ and η , for A-Poisoning in the Diffusionless AB_2 Model with $d_A = d_B = 0$ ^a

	k						
k	$1/10$	$1/2$	1	2	4	10	∞
y_2	0.293	0.393	0.433	0.468	0.489	0.512	0.525
δ	1.97	2.10	2.40	2.70	3.00	3.43	3.70
$-\eta$	1.35	1.45	1.50	1.65	1.75	2.15	2.20

^a Uncertainties in the y_2 (δ and η) are ± 0.0015 (± 0.15). For rough y_1 estimates, see ref 6.

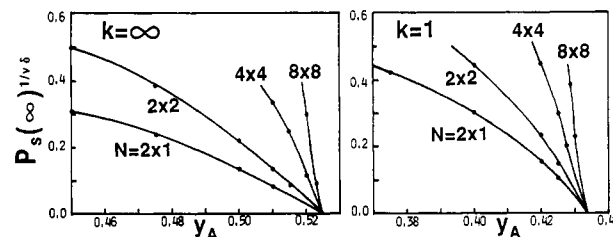


Figure 3. $P_s(\infty)^{1/\delta}$ vs y_A for the $k = \infty$ and $k = 1$ AB_2 models with no diffusion or desorption. Behavior for various initial patch sizes, N , is indicated. We have chosen $\nu\delta = 3.5$ (4) for $k = \infty$ ($k = 1$). Resulting y_2 estimates are $0.525 (0.433) \pm 0.001$ for $k = \infty$ ($k = 1$).

Henceforth we consider the evolution from near-A-poisoned states in the reactive window $y_A \lesssim y_2$. They first evolve toward the A-poisoned state (θ_A increases)—as predicted by MFT—but eventually "turn around" and approach the low- θ_A reactive steady state. The latter process would be traditionally characterized as nucleation-mediated development of the reactive steady state (Figure 1). We argue against this picture below. Instead we think of a near-A-poisoned state as an isolated distribution of small empty patches and focus on the evolution of one such patch. Thus we consider an *oxidation epidemic or spreading* problem of characterizing the evolution of an empty patch in an A-poisoned sea (rather than in a B-poisoned sea as considered above¹⁴). Asymptotic survival (or growth) probabilities, $P_s(\infty)$, are concisely defined here. This contrasts traditional nucleation processes with fluctuating backgrounds as above (where an apparently "dead or disappeared" A blob can always spontaneously remerge).

We use the same scaling relations for the survival probability, $P_s(t)$, and number of empty sites, $N_e(t)$, as above in eq 6, except that now Δ_1 is replaced by $\Delta_2 = y_2 - y_A$. We thus find survival occurs if $\Delta_2 > 0$ with

$$P_s(\infty) \sim \Delta_2^{\nu\delta} \quad \text{and}$$

$$N_e(t) \sim \Delta_2^{\nu(2-\eta)} t^2, \text{ as } \Delta_2 \rightarrow 0 \text{ and } t \rightarrow \infty \quad (7)$$

We find that exponents no longer take RFT values (η even has the opposite sign), and they vary strongly with reaction rate k (Table I). Above we have assumed (and our data confirm) that exponents, but not scaling functions ϕ and f , are independent of the initial patch size, $N \geq 2$, and have chosen $N = 2 \times 1$. Of course, single empty sites ($N = 1$) poison with $P_s(t) = N_e(t) = e^{-y_A t}$. These scaling relations provide a means for y_2 estimation that circumvents difficulties with metastability, described above. One can either appropriately extrapolate the $P_s(\infty)$ to zero (Figure 3) or search for pure algebraic decay in the $P_s(t)$ (Figure 4). Here estimates are enhanced if behavior for larger N is used.

Unlike the traditional epidemic model study (which regards N as fixed), here we are particularly interested in the N dependence of such quantities $P_s(\infty)$. One finds a

(31) Gunton, J. M.; Droz, M. *Introduction to the Theory of Metastable and Unstable States*; Springer: Berlin, 1983.

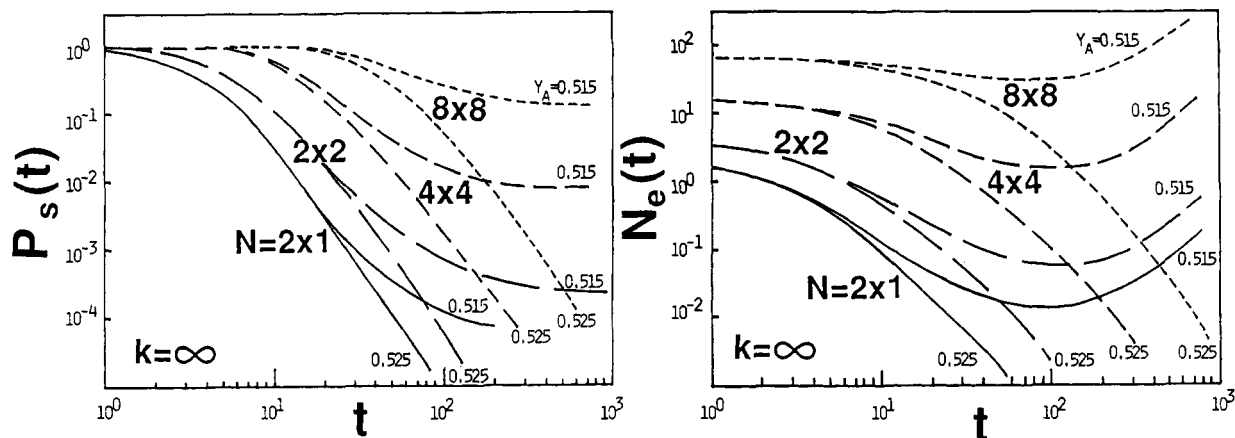


Figure 4. $P_s(t)$ and $N_e(t)$ vs t for the $k = \infty$ AB_2 model with no diffusion or desorption. Behavior for various initial sizes, N , is indicated. Behavior for $y_A = 0.525$ (0.515) at (below) the A-poisoning transition is shown.

rough scaling $P_s(\infty) \sim G(N^\phi \Delta_2)$, where $G(x) \sim x^{\nu\phi}$ (1), as $x \rightarrow 0$ (∞). The small N data, for fixed Δ_2 , show that $P_s(\infty) \sim N^{\nu\phi}$ compatible with the above, and the $\nu\phi = 2.5 \pm 0.2$ (2.2 ± 0.4) for $k = \infty$ ($k = 1$). See ref 13 for a more detailed discussion. However, the basic observation to be made here is that $P_s(\infty)$ increases smoothly with N rather than reflecting existence of a critical size for survival (at least if one is not very close to the transition).

Thus the following picture emerges for $y_A \lesssim y_s$ of the slow development of the reactive steady state from a near-A-poisoned state: most empty patches associated with the initial state "quickly" poison, and thus θ_A increases (an effect enhanced by $\eta < 0$); later the few surviving "epidemic" patches eventually prevail, spreading the reactive steady state across the entire surface thus lowering θ_A . Despite the MFT phase diagram (Figure 1), this process should not be thought of as nucleation limited since there is no distinct critical patch size for survival.

V. Model Modifications: Diffusion, Desorption, Interaction, Etc.

We discuss various model modifications separately.

Diffusion. The analysis of section II shows that the introduction of diffusion into the AB model with $d_A = d_B = 0$ will not effect the resultant poisoning for $y_A \neq y_B$. For AB_2 models with $d_A = d_B = 0$, the main interest has been in the effect of A diffusion (for CO oxidation, often CO but not O is mobile on the surface). Here one sees no effect on the second-order transition; furthermore the first-order transition is preserved but y_2 is shifted upward due to the enhanced reactivity and reduced propensity for cluster formation of the A species. Its maximum value of $2/3$ is simple determined by stoichiometry.^{3,20} Diffusion of the B species dramatically decreases y_1 (through reduction of the empty-pair density) and eventually removes the B-poisoned phase.⁹ This recovery of MFT behavior should be expected from our previous comments.

(Nonreactive) Desorption. Clearly desorption of a species removes the possibility of an associated completely poisoned state. Here we consider only the AB_2 model, where low desorption rates still produce multiple steady states with the traditional van der Waals type structure in MFT treatments (Figure 1).^{6,8} However, there exists a *critical desorption rate* (analogous to a critical temperature) above which a unique steady state is found.⁸ Thus one expects microscopic AB_2 models to exhibit first-order A-poisoning transitions only for sufficiently low desorption rates. Simulations for "higher" desorption rates show broadening of the region of transition from high to low reaction rate; the reaction maximum is found at higher y_A .^{3,20}

Pairwise Interactions, J . There has been one simulation study where all microscopic processes are influenced by interactions through Arrhenius-type rates.²⁰ If $J_{AA} = J_{BB} < 0$ are attractive, then the reactive state always disappears below some critical temperature. If $J_{AA} = J_{BB} > 0$ are repulsive, the above still occurs if $J_{AB} > J_{AA}$ is stronger (corresponding to the disappearance of a mixed phase in the corresponding nonreactive system), but a reactive phase always exists for weaker $J_{AB} < J_{AA}$. In such models the reaction rate effectively depends on coverage, so based on MFT studies there is a potential for self-sustained oscillations.¹ These have not been observed to date (for these models).

Eley-Rideal Mechanism $A + B(\text{ads}) \rightarrow AB + E$. The main effect of this process for desorptionless models is to replace the B-poisoned phase with a reactive phase.^{6,22} For the diffusionless AB model with $d_A = d_B = 0$, there is a continuous transition from the reactive phase to the A-poisoned phase at $y_A = 0.4922$.²² For the AB_2 model, MFT studies reveal multiple steady states,⁶ and a corresponding first-order transition to an A-poisoned state is found in simulations; y_2 is reduced.²²

Dimer Adsorption Mechanism. There has been little appreciation of the strong sensitivity of AB_2 -model behavior to the choice of B_2 -adsorption mechanism. After randomly picking an empty site, one can either randomly choose a second site from among all neighbors (adsorbing B_2 only if both are empty), or randomly choose from among only empty neighbors (if one or more exist).³² The first is the standard choice assumed above and used almost exclusively. Since it is equivalent to simultaneously picking pairs of sites (and adsorbing only if both are empty), it can be associated with a horizontal "transition state". The second "end-on" mechanism that is naturally associated with a vertical "transition state" is more "persistent" and less sensitive to adlayer statistics. (It produces higher B coverages in nonreactive competitive monomer-dimer adsorption.³²) Thus one expects behavior more like the AB model. Indeed, the "end-on" ZGB model has a narrow reactive window ($y_1 \approx 0.635$, $y_2 \approx 0.655$), which decreases in width as $k \rightarrow 0+$ (the Voter model limit where $y_1 = y_2 = 1/2$). Note that in a refined model where the B_2 dimer somehow always succeeds in adsorbing, after picking one empty site, one must have $y_1 = y_2 = 2/3$ (for finite or infinite k).

Self-Sustained Oscillations. As noted in section II, additional nonlinear feedback must be introduced into the above models to produce such oscillations. Clearly a synchronization mechanism is also needed to bring spa-

tially separated oscillating regions into phase with each other.³³ For CO oxidation on Pt(100), the source of the feedback is a surface phase transition, which dramatically affects the O₂ sticking probability.³⁴ A detailed microscopic (lattice model) simulation of this process (without diffusion) did indeed produce oscillations and chemical waves.³⁴ The latter did not have the same length scale as the waves observed in the experiments, this scale being determined by the diffusion rates.³⁵ No doubt, a variety of microscopic models exhibiting oscillations could be constructed. Feedback could occur through the dependence of the O₂ (or B₂) sticking coefficient on subsurface O (B),³³ or perhaps just in some simpler way on system parameters (coverages). Finally we note that oscillations and even chaotic behavior has been observed as a finite-size effect in AB-type models.³⁶

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VI. Conclusion

A sophisticated understanding is emerging of reaction kinetics and kinetic phase transitions in microscopic lattice-gas models for surface reactions where diffusion does not play a dominant role. Mean-field-type treatments are useful in elucidating behavior near first-order transitions, but their quantitative predictions should be viewed with skepticism. A detailed characterization of critical behavior near such transitions is provided by Monte Carlo simulation using, for example, finite-size scaling techniques, and concepts from the theory of critical epidemics (at least for processes with completely poisoned states). A theory of nucleation for nontrivial reactive metastable states has yet to be developed.

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